New formulation of the lattice cluster theory equation of state for multi-component systems

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A B S T R A C T

The molecular structure or short chain branching of chemical compounds is known to have a strong impact on their thermodynamic behaviour. For example the vapour pressure of isomeric alkanes is increased with branching, but also the behaviour of more complex species and mixtures of them can be quite sensitive to molecular architecture. Usually, thermodynamic properties like equilibria or densities are modelled by the use of equations of state, of which the physically based ones, like the Statistical Associating Fluid Theory (SAFT) family have become popular in the past two decades due to their ability to accurately describe a rich variety of thermodynamic properties. However, these theories are not capable of including branching effects on an *a priori* basis. Recent advances in the application of lattice cluster theory have shown that this theory is capable of describing isomeric effects for pure alkane isomers, namely the rising vapour pressures with stronger branching. The description of these effects is extended here to multi-component systems, while retaining the simple functional form of a series expansion. Moreover, the original theory is simplified using some graph invariants, without loosing any thermodynamic information.

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1. Introduction

Today polymers play a crucial role in industrial and scientific applications ranging from the use of super absorbing polymers [1] (*e.g.* in diapers) to the use of aerogels as dust collectors in the search for interstellar dust [2]. For processing and application purposes the knowledge of the polymers' thermo-physical properties is important. For example the solubility of the polymer with different molar masses in its monomer is a key aspect of the production process since the reaction would stop if the polymer starts to demix with its monomer. This does not have to be a negative aspect and can even be used to stop the polymerization at a certain molar mass [3], if the phase behaviour is well known. However, the thermodynamic properties of the polymer depend strongly on its molecular weight (MW) and architecture, as well as its chemical composition.

Of these dependencies the MW-dependence has been addressed thoroughly by many approaches over several decades. These approaches lately include physically based equations of state like the statistical associating fluid family (SAFT-family) [*e.g.* 4–10] (see Tan et al. [11] for a recent review). Most of the SAFT versions, however, cannot predict the influence of molecular structure on the thermodynamic properties, which is desirable for example when describing polyethylene solutions or blends, because usually in the polymerization process there is a strong polydispersity with respect to MW, as well as short-chain branching. The impact of short chain branching can be seen from Fig. 1, where the cloud point of pressures of linear and branched polyethylene (PE) in ethylene at fixed temperature for polymers of similar molecular weight is shown. The cloud point pressures reduce by about 40 MPa for the branched polyethylene. Furthermore, novel materials like dendritic or hyper-branched polymers show a strong impact of branching on physical properties [12–15]. Therefore SAFT versions that can model branching have been developed [16–18] using the second order thermodynamic perturbation theory (TPT2) by Wertheim [19–22]. These are limited due to the fact that they only allow tetramer units as branching points or treat pentamer units simply the same as tetramer branching points. Also, with these theories, it was not yet possible to model the vapour–liquid equilibrium (VLE) and lower critical solution (LCST) behaviour with the same set of parameters for hyper-branched polymer solutions [17]. All these approaches use the TPT2 approach and are thereby limited to local correlations between a maximum of three segments. A different approach is the use of
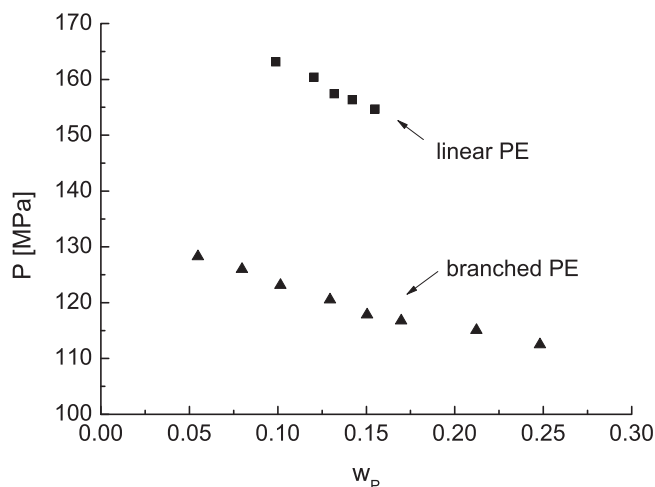
Fig. 1. Experimental [33] cloud point pressures of linear polyethylene (squares) and branched polyethylene (triangles) of similar molecular weight (weight average molecular weight is about 54–55 kg/mol) in ethylene at T = 423.15 K over polymer mass fraction.

group contributions [9,23–31] where different groups have different sizes and interact through different interaction energies. This course of action, however, demands the fit of these parameters to a large amount of data and cannot distinguish between different positions of the group on the molecule. For a more detailed description of theories used in describing polymer solutions and blends please see Wolf and Enders [32].

It is possible to take the MW-dependence and the architecture dependence into account by use of the lattice cluster theory (LCT) developed by Freed and co-workers [34–51] taking into consideration local correlations of up to four monomer segments. This lattice based, incompressible model was extended to account for pressure effects by Dudowicz and Freed [39] and was recently simplified for pure compounds, yielding the LCT equation of state [52] (LCT-EOS). LCT-EOS was successfully used to model the vapour pressure differences due to isomerism by Langenbach and Enders [52]. The reason for the simplification is that the original equations by Dudowicz and Freed are quite unwieldy. A further analytical rearrangement, using some graph invariants derived by Nemirovsky et al. [44], resulted in a much less complex expression for the free energy of binary compressible systems by Browarzik et al. [53], which was successfully applied to the calculation of binary high pressure LCST behaviour, as well as vapour–liquid and vapour–liquid–liquid phase behaviour of hyper-branched polymer and solvent. The simplification to cases of one, two or three compounds is often done, if actual phase equilibrium calculations with the LCT or LCT-EOS are performed [53–60], because it is possible to avoid numerical pitfalls this way. These pitfalls may result from the heavy summations in the original equations [39]. Sometimes, approximations, such as the incompressible, high molecular weight or light branching limits are used in order to further simplify the original expressions of Freed and co-workers. For example, Arya and Panagiotopoulos [61] examined the incompressible limit, comparing LCT to Monte Carlo simulations of linear and branched molecules. Though taking into consideration the full theory up to second order [39], using also the corrections by Dudowicz et al. [62], Arya and Panagiotopoulos [61] conclude that the architecture influence is not predicted to the full extent by LCT. This is partially due to their choice of the lattice coordination number as z = 26 for a cubic lattice. In contrast to that, Browarzik et al. [63] find a strong influence of architecture on the phase behaviour of polymers in accordance with experimental data of Kleintjens et al. [64] for incompressible solutions of polyethylene in diphenyl ether using z = 6. The higher coordination number of Arya and Panagiotopoulos [61], the inverse of which is one of the expansion variables, most probably reduces the influence of architecture on the free energy. This is expected, since in the infinite coordination number limit, the Flory–Huggins theory [65,66] is recovered from LCT. Freed and Dudowicz [67] propose a limiting case, where both the limit of incompressibility and the high molecular weight limit are taken. The limit of light branching is implied by the calculation of geometrical coefficients from the number of branching points only, as proposed by Nemirovsky et al. [44]. Some other authors derive semi-empirical expressions trying to mimic the behaviour of LCT, but using simpler algebraic equations [e.g. 68,69]. However, even though limiting cases and theories approximating LCT are useful to alleviate the complexity, a complete version, yet simplified to the fullest possible extent without losing thermodynamic information is desirable.

This paper is concerned with the reasonable algebraic simplification of the compressible multi-component lattice cluster theory. In order to allow multi-component systems, the reduced lattice interaction energies $\tilde{\varepsilon}_{ij}$ have to be contracted with their pure compound pendants $\tilde{\varepsilon}_{ii}$ and $\tilde{\varepsilon}_{jj}$ into the exchange interaction energy $\Delta\tilde{\varepsilon}_{ij} = \tilde{\varepsilon}_{ii} + \tilde{\varepsilon}_{jj} - 2\tilde{\varepsilon}_{ij}$ yielding a clearer separation between the pure compound effects and the effects of mixing. Furthermore, it is possible to reduce the number of combinatorial factors by use of the graph invariants of Nemirovsky et al. [44]. Together, these simplifications lead to 26 contributions in the residual free energy of compressible multi-component systems, which is a major simplification compared to the 102 original contributions by Dudowicz and Freed [39]. Hence, the new equation of state is more suitable for engineering purposes. The new multi-component LCT-EOS is presented in this paper. Some example calculations are shown and compared to experimental data.

2. Lattice cluster theory equation of state

The LCT derived by Freed and co-workers [34–51,70] is a lattice theory that enables the inclusion of structure directly into the equation of state. However, the original form of the equations involves a massive amount of summations, which makes it prone to numerical error, if used directly. Typically this problem is avoided by setting the number of compounds to one [43,52,59], two [e.g. 40,43,59] or three [56,58] components and rearranging the terms. Recently Langenbach et al. [53] have shown that for the compressible case with two components